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Conversion of Cattle Manure Into Useful Products

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CONVERSION OF CATTLE MANURE INTO USEFUL PRODUCTS

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The purpose of the project was to design and build a pyrolysis apparatus for cattle manure and to investigate the potential uses of the pyrolysis by-products. A pyrolysis machine of semi-continuous feed capabilities was designed and built. Various conditions of pyrolysis treatments were investigated and their influence on the amount and composition of the by-products determined. High carbon residues were found to require lower pyrolysis temperatures. The carbon content of these residues appeared to be unaffected by the geographic location of the original manure. Contact with interested parties and appropriate industries who could be prospective users of each of the products was initiated to obtain their technical expertise in evaluating these products. The pyrolysis by-products seem to have some potential industrial applications. These by-products include the solid residue, an oil fraction, and an aqueous fraction. The solid residue may serve as a carbon black substitute or as a filler material in rubber, ink, and paint. The aqueous fraction collected during pyrolysis has been evaluated for fertilizer applications.

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SECTION I

INTRODUCTION

There is a trend toward confining animal feeding operations thus producing large amounts of orgniac waste and concentrating them in a small area. The disposal of such large quantities of animal waste in a small area creates problems of odor and water pollution. Due to low efficiency and high cost of handling, it is no longer economical for manure to be transported and used as fertilizer. Some alternative method of disposal is needed. A further attraction is the possible utilization of waste matter to produce useful products. These will alleviate the ever increasing burden which is placed upon our natural resources.

In California, it is estimated that there is as much as 9×10^6 kilograms of cattle manure produced per year and these are concentrated in a few small acreages. In 1971, a method was partially developed at UCLA for the conversion of cattle manure into useful products. A very small apparatus was employed. Manure was decomposed to its chemical constituents at an elevated temperature in an atmosphere which was oxygen deficient. The gases and vapors of the pyrolyzed manure ash was a black, odorless, granulated solid and was named Treated Cow Dung (TCD).

The objectives of this research project may be generally arranged into three categories:

1. The design, construction, and actual performance of equipment for manure dehydration and pyrolysis. This aspect of the research was designed to provide relevant engineering data concerning manure pyrolysis and to furnish samples for the evaluation of the resulting products (see 2 below).

2. The evaluation (by the appropriate industry) of the various secondary products which may be produced from manure pyrolysis. These secondary products are derived from one of the three primary by-products of the pyrolysis treatment (i.e., TCD and oil and aqueous fractions). These secondary products should have the following features: 1) they must be capable of utilizing large quantities of the manure, 2) they should be of comparable quality and value to

presently existing commodities, and 3) they should be economically feasible to manufacture. A flow chart of various applications for by-products of pyrolyzed cattle wastes is shown in Figure 1.

3. The contact of various parties who may aid or be interested in the research program. This includes the contact of feedlots and appropriate industries who may either be able to provide valueable services (e.g., supply manure, evaluate samples) or benefit by an information exchange

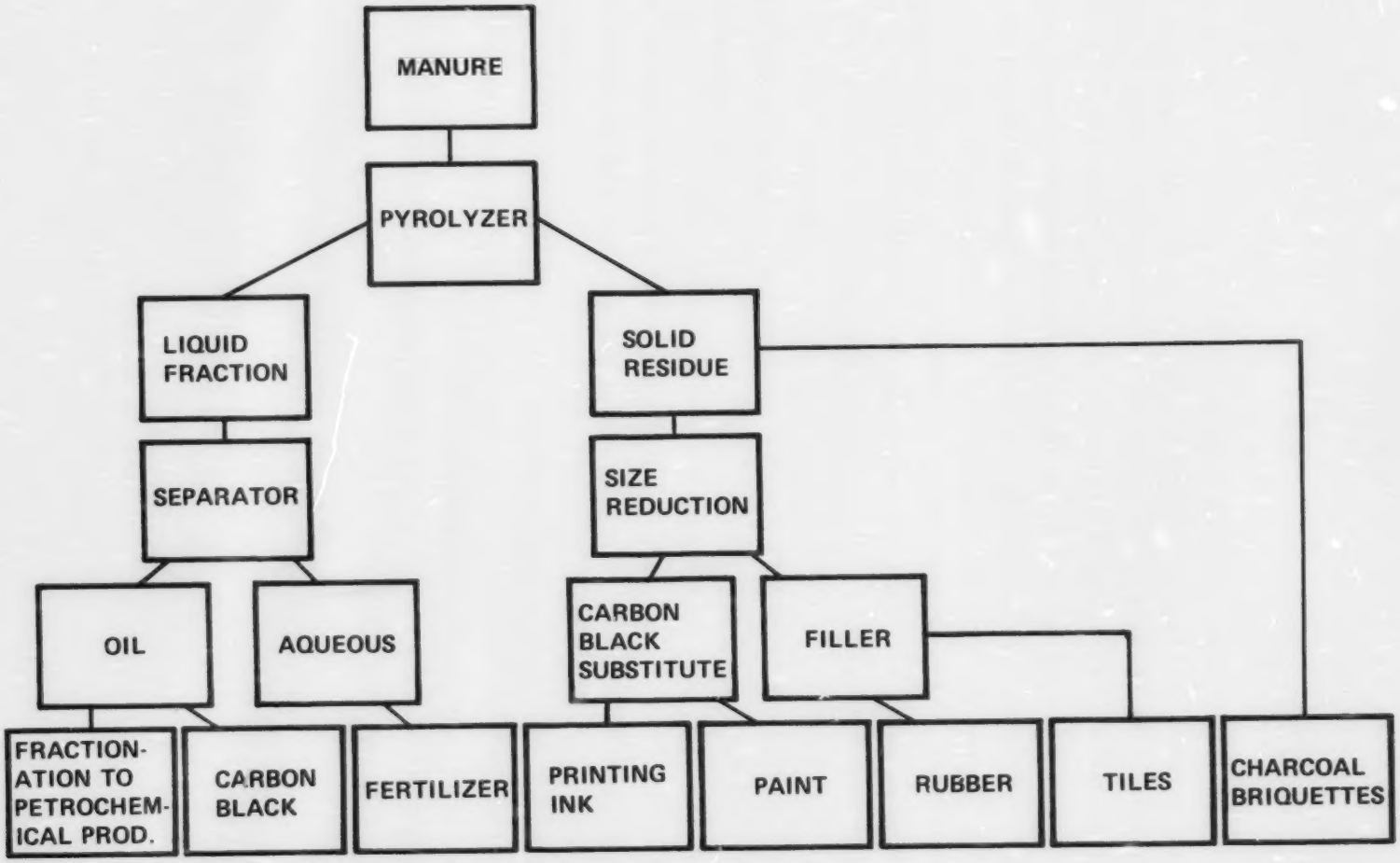


Figure 1. Applications of the By-Products of Manure Pyrolysis.

SECTION II

SUMMARY

An apparatus for pyrolyzing cattle manure was designed and built, and the potential product applications which utilize the pyrolysis by-products were investigated. The pyrolysis equipment has a semi-continuous feed capability. Various conditions of pyrolysis treatments were studied and their influence on the amount and composition of the primary by-products was determined. A highly carbonaceous solid residue was obtained at lower pyrolysis temperatures and the carbon content was unaffected by the geographic location of the original manure. Mass balance calculations were performed and accounted for the distribution of the chemical constituents of the manure among the primary by-products of pyrolysis.

Three primary by-products were obtained from the pyrolysis of cattle manure: a solid carbonaceous residue, an oil fraction, and an aqueous portion. Numerous secondary products may be derived from these primary by-products. The solid residue was used as a carbon black substitute and filler in printing ink, paint, rubber, tiles and charcoal briquettes. The oil was fractionated into carbon black while the aqueous portion was evaluated for fertilizer applications. Appropriate industries who could be prospective users of each of the products were contacted and helped in the evaluation of these materials. The most viable application appears to be the use of the solid residue as a carbon black substitute. A brief cost analysis concerning the production of this material was performed.

SECTION III

CONCLUSIONS

Cattle manure can be utilized in many useful products by pyrolyzing the manure and using the various by-products either by themselves or by incorporating them with other materials.

The optimum pyrolysis temperature depends upon the desired end product. For product applications where the carbonaceous residue, hereafter referred to as Treated Cow Dung (TCD), is used for a carbon black substitute, a lower pyrolysis temperature is used to retain more carbon in the ash.

In cases where high carbon content is desired, the TCD possesses fairly consistent carbon concentrations, regardless of geographic location.

When pyrolyzed ash is substituted for carbon black in product applications, the size of the powdered ash is significantly larger than that of carbon black and further size reduction is necessary.

Ink and paint of acceptable quality can be made with pyrolyzed cow manure ash in partial substitution for carbon black.

Crude oil condensed from the pyrolysis of manure can also be used to produce carbon black of quality equal to those used in industry.

For large volume applications, the use of TCD as a filler in ceramic tile holds promise. Tiles can be produced which are equal in strength and durability to commercial tiles.

The water fraction holds promise as a fertilizer carrier when upgraded with primary nutrients.

TCD has been successfully used as a filler and colorant in rubber. The optimum characteristics for this application are, at present, not known.

TCD with high carbon content has been qualitatively assessed as a principal constituent of modified charcoal briquettes.

SECTION IV

RECOMMENDATIONS

At the inception of this research program, it was hoped that both sufficient data for evaluating the technical factors and the economics of manure pyrolysis and sufficient pyrolysis products for complete application evaluation could be produced. Such additional data and additional samples can only be made available from the operation of a small pilot plant of approximately 9.08×10^3 kg per day capacity. the preliminary results and analyses provided by the industrial contacts were encouraging in many respects. They stress, however, that considerably larger sample sizes are required in order to perform a thorough industrial-scale evaluation. Thus, a larger scale research program for this essential intermediate step is recommended. This program will not only supply the larger sample quantities involved for thorough evaluation but also enable the pyrolysis apparatus to be further adapted towards economic production methods. For example, continuous pyrolysis could be implemented. Certain equipment features could be improved (e.g., use of cold traps should be modified or a high temperature seal for moveable parts developed).

In the product field, a more critical analysis concerning the fractionation and combustion of crude oil is needed. Due to the energy shortage, this fractionation is of utmost importance. For the other items such as TCD briquettes, tiles, and carbon black substitutes, detailed economic analysis should be performed to determine which combination of products offers the best return on investment.

SECTION V

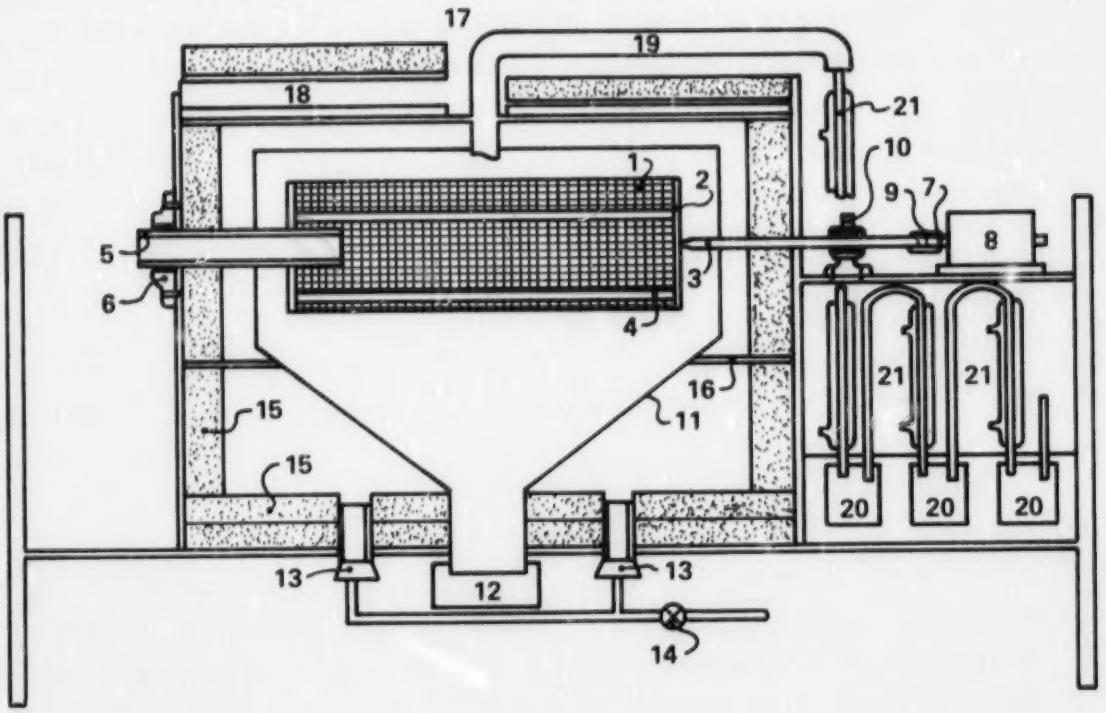
PYROLYSIS OF CATTLE MANURE

This section considers all the experimental aspects concerning the design and operation of the manure pyrolyzer. The overall objective here was to obtain relevant engineering data about the pyrolysis mechanisms and to provide sufficient quantities of the pyrolysis by-product for evaluation purposes. The pyrolyzer design, operating procedure, and experimental results are discussed separately within this section.

DESIGN AND CONSTRUCTION OF APPARATUS

The process for manure treatment involved a semi-continuous pyrolyzing unit (Figure 2). The pyrolyzer consisted of an inner rotating cylinder (0.3 m by 0.3 m) constructed of Type 304 stainless steel, No. 10 mesh screen. The end plates of the cylinder were machined from 1.27-cm, Type 327 stainless steel. One of the end plates of the rotating screen drum was mounted on an axis connected to the motor drive. The end plates were supported by three rigid cross beams, which had many attachment notches for varying the overall cylindrical screen size. The other end plate was mounted on a tube supported by a 8.9-cm adjustable bearing. This tube provided the entrance for the semi-continuous feed. The end of the feed tube had provisions for a semi-continuous piston loader which was not installed due to time limitations. A removable cap was used instead. The motor drive shaft was connected to the motor by means of a rubber joint to allow for mismatches in concentricity.

The shaft itself was supported by another 2.54-cm adjustable bearing. The screen was housed within an airtight, welded, rectangular enclosure with a removable faceplate which enabled ease of cleaning and maintainance and screen adjustments. The storage container and a slide plate that enabled periodic observations of the progress of pyrolyzation. The pyrolyzer was gas-fired using adjustable gas jets. Gas pressure was measured in inches of H_2O by a manometer to insure consistent heating rates for pyrolysis. A gas valve was installed for gas cutoff of two burners for temperature maintenance. The gas



(1) No. 10 Mesh Screen
(2) End Plates
(3) Axis
(4) Cross Beam
(5) Feed Tube
(6) Adjustable Bearing
(7) Motor Drive Shaft
(8) Motor
(9) Rubber Joint
(10) Adjustable Bearing
(11) Housing
(12) Storage
(13) Gas Jets
(14) Valve
(15) Bricks
(16) Frame
(17) Flue
(18) Drying Chamber
(19) Condensing Pipe
(20) Condensing Jars
(21) Glass Tubes

Figure 2. Plan View of Pyrolysis Unit.

burners were located on the bottom of the outer furnace. The rectangular, stainless steel pyrolyzer unit was enclosed in refractory bricks held together by an angle-iron frame to prevent unnecessary heat loss. The pyrolyzer unit was supported by an angle-iron frame resting on the outer furnace. Two adjustable ventilation-exhaust flues were located on top of the outer brick furnace to aid heat retention control. A small chamber on top of the outer furnace allowed predrying of wet manure. The exhaust was directed into a fumehood.

A 5.1-cm pipe at the top of the stainless steel pyrolyzer drew the vaporized fraction of the manure during pyrolysis. The 5.1-cm pipe led to a series of 3 condensing jars with interconnecting water-cooled glass tubes. Draw was provided by a small vacuum and a small air release valve was attached before the vacuum to prevent overloading.

The roof of the outer furnace was supported by angle iron and ceramic plates.

EXPERIMENTAL PROCEDURE AND RESULTS

A flow chart of the total manure treatment operation is shown in Figure 3. The first step in pyrolyzation was to determine water content of the sample to be pyrolyzed. The samples were first placed in a small preheating chamber on top of the pyrolysis machine. A predetermined batch (usually 1,000-2,000 grams) was loaded through the feed tube into the pyrolyzer.

Temperatures were checked every five minutes to insure that the heating rate was identical for each sample. The heating rate is shown in Figure 4. Once the desired pyrolyzation temperature was reached, the motor drive rotated the inner stainless steel drum. The rotation, together with the pulverizing action of the alumina balls inside the drum, reduced the larger pieces of cow manure and allowed increased surface reaction. Once the manure was pyrolyzed, the pulverizing action of the alumina balls forced the reacted ash through the stainless steel mesh, where it then dropped into a storage container. The storage container was located under the heating zone of the furnace to prevent further pyrolyzation. Small samples could be taken during pyrolyzation to check its progress without affecting the process. As soon as vapors could be observed in the primary condensing tube, the small vacuum was turned on to draw the

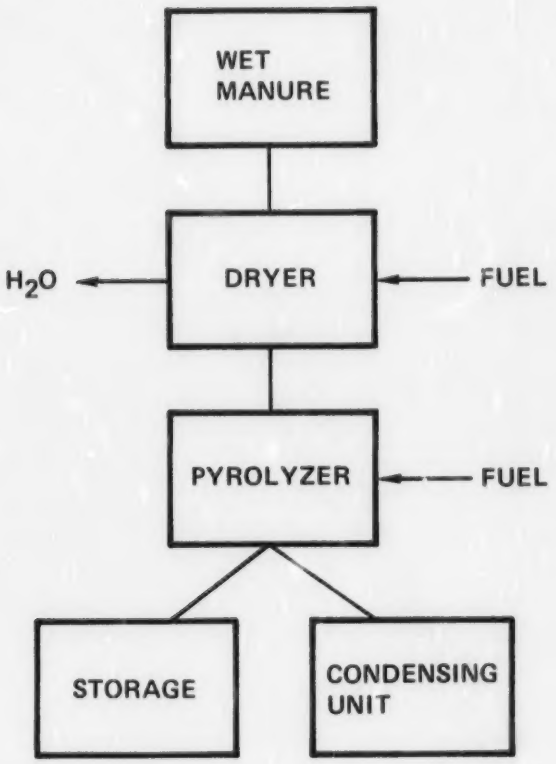


Figure 3. Flow Chart of Manure Pyrolysis Operations.

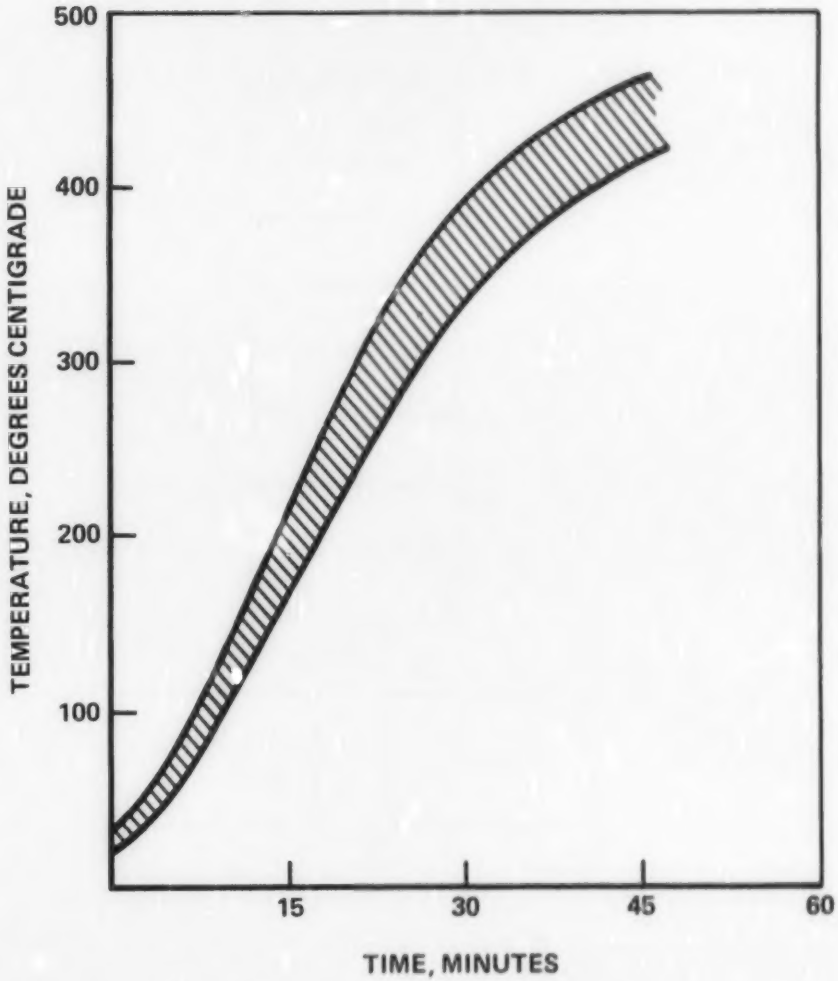


Figure 4. Controlled Heating Rate Schedule for Pyrolysis Operation.

vapors through the set of 3 condensers. The minimum vacuum needed to pull the vapors through the system was used. The purpose of the minimum vacuum was to get maximum condensation while preventing an overload on the vacuum. When the vapors had stopped emanating, the run was considered complete. The motor drive was continued to ensure that all pyrolyzed ash had passed the stainless screen. Ventilation flues were opened for cooling. The pyrolyzed ash was left in the storage container for a minimum of 30 minutes to ensure cooling to prevent spontaneous combustion once it was exposed to air. The jars containing the condensed aqueous fraction could be removed immediately for weighing. The aqueous fraction was separated into its oil and water components by centrifuging. The specific results of the various pyrolysis experiments are discussed below.

Table 1 lists the more significant pyrolysis results. The effect of different time and temperature conditions on the effective yield is also shown. Generally it was found that for a relatively low temperature of pyrolysis, there was more ash produced, while at a greater pyrolysis temperature, there will be a larger aqueous fraction. This result is also shown in Figure 5. During high temperature pyrolysis, more carbon was fractionated from the manure and condensed into the oil from the aqueous fraction. For applications where TCD was

Table 1. CONDITIONS FOR PYROLYSIS AND CORRESPONDING YIELDS (Pamona Manure)

Load (grams)	Temperature (degrees centigrade)	Time (hours)	Solid Yield (%)	Liquid Yield (%)
1500	225°	3.0	53.5	32.1
1500	240	2.5	45.2	11.4
1000	300	2.5	46.5	27.6
1000	325	2.5	25.0	19.9
1500	325	2.5	41.3	16.3
1000	350	2.5	34.8	19.1

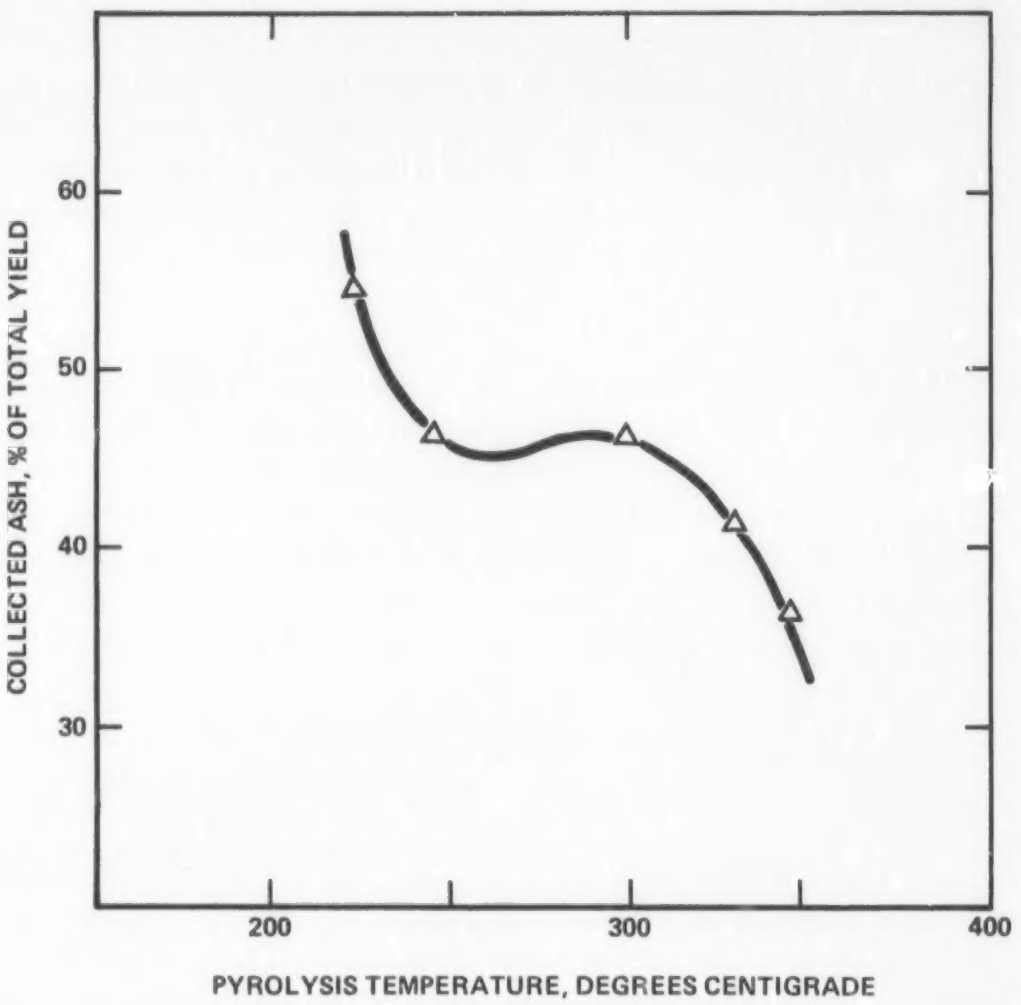


Figure 5. Influence of Pyrolysis Temperature on the Amount of Ash (or TCD) Collected.

used as a black pigment or a filler, pyrolysis was carried out at relatively low temperature (300°-325° C) since more carbon was left in the ash at these conditions.

The time of predrying had substantial effect on the total water fraction generated during pyrolysis. Predrying decreased the amount of water contained in the aqueous segment (moisture content of the received manure samples varied from 14 to 25 weight percent). Increased water content affected the initial rise in temperature. For these samples, an increase in gas pressure to the burners was necessary in order to obtain the desired heating rate.

A typical chemical analysis of both the pyrolysis by-products and the initial manure sample is shown in Table 2. Similar results were obtained with all the manure samples investigated in this work.

Table 2. CHEMICAL ANALYSIS OF INITIAL AND PYROLYZED MANURE SAMPLED

	% Carbon	% Hydrogen	% Nitrogen
Raw Manure	23.82	3.80	1.85
Oil Extract	54.71	7.78	5.38
Water	0.74	----	0.27
Ash	30.07	1.49	----

DISCUSSION

The entire pyrolysis treatment was subjected to a mass balance analysis. In this procedure, all chemical constituents present before and after treatment were compared. Naturally, complete agreement was desired. This analysis was valuable because it described the distribution of the various elements. Pyrolysis treatment schedules may then be adjusted to obtain various distributions.

The results of a mass balance calculation for the present study are shown in Table 3. Similar results were obtained for all manure samples. This particular run was selected because of its fairly high efficiency (i.e., 91% efficiency

or 9% stack loss). The objective of Table 3 is to have item (a), the chemical constituents of the raw manure, compare favorably with item (e), the total chemical constituents of the pyrolysis by-products. This balance is summarized in item (f), the accountability ratio (e/a). Good agreement is obtained for carbon (91%). This is probably the most important element for product application purposes(i.e., oil, carbon black substitute as given in Section V). Only fair agreement was found for hydrogen (66%), while poor results were observed for nitrogen (39%). These values for hydrogen and nitrogen were undoubtedly due to the stack loss. Other mass balance calculations using pyrolysis treatments with even greater stack losses (i.e., greater than the 9% value in Table 3) exhibited correspondingly similar results. That is, good agreement for carbon but even worse values for hydrogen and nitrogen than were observed here.

Table 3. MASS BALANCE

(per 1,000 gms, 91% efficiency)

	C(gm)	H(gm)	N(gm)
a) Raw Manure	238	38	18
b) Oil Extract	62	9	6
c) Water	2	8*	1
d) Ash	152	8	-
e) Total (b), (c), (d)	216	25	7
f) Accountability Ratio (e/a)	91%	66%	39%

Thus, it is reasonably certain the stack losses include water vapor and a volatile fraction (containing nitrogen) which were not condensed. These losses are present because of the draft utilized in the system. The draft provided by the vacuum was needed to draw out the vapors. Even with the draw, much of the hydrocarbons were burned within the pyrolysis chamber before being drawn and condensed. Without the vacuum, very little oil would be condensed.

The amount of the stack loss was considerably greater than expected. The primary reason was an inefficient condensing system. Even with the modified

condensing system, an average 10-percent stack loss was generally observed. A variable temperature run was made in which various temperatures were equilibriated until no additional condensate appeared. Intervals of 50° C in a range of 200° C to 400° C were tried. The loss of condensable vapors were close to 50% indicating that much of the vapor fraction was being burned in the pyrolysis chamber.

Variable loads of manure ranging from 500 grams to 2,000 grams were also investigated. For the larger loads, longer pyrolyzation times were not required. The initial heating was slower in the beginning but was adjusted to follow the heating curve by varying the amount of gas. It was previously mentioned that the chemical analysis of the pyrolysis by-products (Table 2) was similar for all the manure samples tested. In Table 4, a comparison of the hydrogen and carbon contents of TCD samples from this and other studies was presented. The localities are indicated. The agreement is excellent.

Information such as this is important for industrial applications. The implication here was that fairly uniform carbon contents of TCD may be obtained from pyrolysis regardless of geographic location. The notion that properly treated manure contains a certain equilibrium content of carbon was strongly suggested. Although this equilibrium content depends upon processing conditions[5], other aspects such as feed ratios are of secondary importance as far as the carbon content of TCD is concerned. This result was quite encouraging and should be of interest for future pilot plant operation.

Table 4. COMPOSITION OF TCD FROM DIFFERENT LOCALITIES

	Brawley, Calif.	Colorado	Ohio
C	30.56%	24.28%	30.07%
H	1.19%	1.16%	1.49%

SECTION VI

PRODUCT APPLICATIONS OF PYROLYSIS

BY-PRODUCTS

This section considers the various efforts made towards evaluating the products which may be fabricated using the pyrolysis by-products. The by-products are TCD, oil, and the aqueous fraction. In some instances (e.g., TCD) several viable products have been investigated while in other cases (e.g., the aqueous fraction), only one application has become evident. Each of these aspects are considered in detail.

PRODUCT APPLICATIONS OF TCD

TCD is generally used for two purposes: as a carbon black substitute and as a filler material. In paint, ink, and rubber applciations, it serves in both capacities. The tiles utilize TCD strictly as an inexpensive filler. Each of these applications are discussed in detail below.

Ink

The pyrolized manure ash can be used as a carbon black substitute and filler in newsgrade black ink. The preparation of the ash for this purpose involves particle size reduction by ball-milling. The TCD ash is then mixed in an ink mill with other additives in the following ratio:

Mineral Oil	65%
Resins & other body modifiers (heavy linseed oil)	15%
CB (Commercial carbon black)	10%
TCD	10%
Toner (added later 1/2-2w/%)	
Drier (added as needed, 1/2-2w%)	

By substituting ball-milled TCD for up to 50% of the total carbon black content, ink of a satisfactory quality can be produced. Industrial evaluation was made by three commercial operations: Gan's Ink (an ink manufacturer), Geiger Brothers (the printers of the Farmers Almanac), and Sinclair Paints.

The general conclusion reached by these industrial users is that TCD carbon black ink can definitely be used in certain specific applications. Because of its low tinting quality (very low black jetness) TCD inks may only be used when quality inks are not necessary (newspapers, flyers, etc.). Unfortunately, TCD with high carbon content did not significantly improve the tinting. The reason for this is that the ash content of TCD is considerably greater than that of the carbon black it is replacing.

Another problem is that of the TCD particle size. Carbon black powders produced by commercial processes for use in ink are on the order of millimicrons whereas the minimum size of TCD, obtained by ball milling, is one micron.

The studies concerning the influence of grinding time on the particle size of TCD is shown in Figure 6. Because of the particle size limitation, only the minimum-sized particles were supplied for evaluation. From the above discussion it is evident that if finer-sized particles could be obtained, better inks could be fabricated and the use of extra body modifiers would not be necessary. Finer particle sizes are desired because it increases the surface area thus improving wetting characteristics.

Another problem of large particle sizes is that the ink will not adhere to a high-speed roller so that ink droplets will fly off the roller in a mist.[3] Caking due to dry ink will also occur. Furthermore if any sand is present in the TCD (sand may be inadvertently collected from the pens), its inherent grittiness makes the ink not amenable to high-speed applications. The soft lead type will be quickly worn out.

The more specific comments regarding the ink application are given as follows: Mr. R. A. Geiger, the editor of the Farmers' Almanac, has used our ink on a Miehle Vertical Press. The initial worry of the grittiness and large size

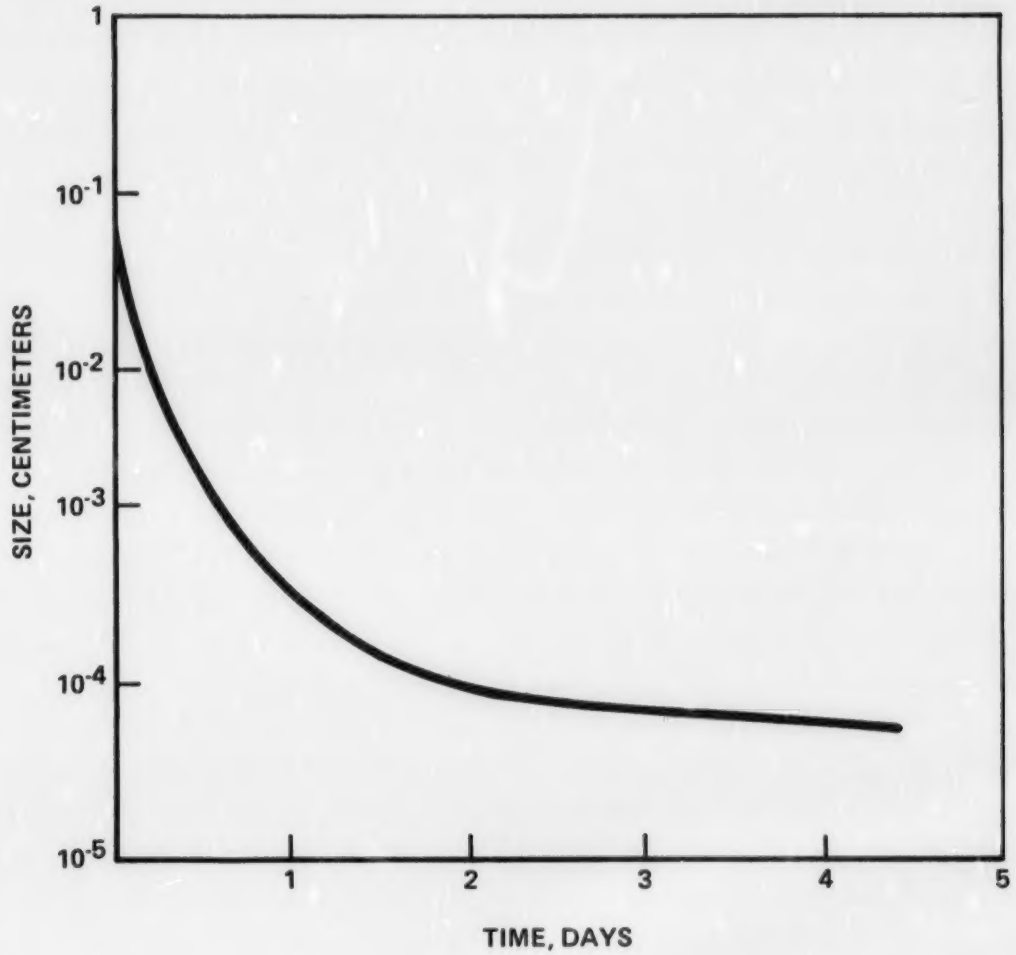


Figure 6. Effect of Grinding Time on the Particle Size of TCD. (Grinding by Ball Mill).

did not prove to be an important factor in the overall use of the ink. The problem encountered was that of the body of the ink being too thin. This caused the ink not to lay on the printed sheet quite as well as desired. In general then, the TCD-based ink appears to have some promise. However, Mr. Geiger has informed us that a final evaluation can only be made with considerably larger samples of TCD.

The research labs of Sinclair Paints evaluated the TCD ash for tinting strength. They reported that the ash had approximately 5% the tinting strength of carbon black. This conclusion was essentially confirmed by Gans Ink.

In conclusion then, further research is needed to evaluate inks made with mixtures of varying proportions of carbon black to TCD. Further information on the possibility of increasing toning is necessary. It would appear that there is a real opportunity here to utilize TCD.

Paint

Pyrolyzed manure ash can also be used as a filler and color pigment in paint. The pyrolyzed ash was substituted for lampblack in the paint. As in the case of the ink application, the pyrolyzed ash sample was milled to approximately one micron.

Samples of the TCD ash were sent to the research laboratories of Sinclair paint for evaluation. Preliminary evaluation indicated that the carbon content of the TCD must be in excess of about 30% in order for the TCD to be useful for black paint. Secondly, average particle size must be less than one micron. Samples containing the greatest carbon content (30%) were sent. Two samples of paint were made from the milled TCD ash. The first sample was prepared by substituting 25% of the TCD for the normal quantity of lampblack. A test paint was fabricated. The objective here was to test the pigmentation quality of TCD. Sample 2 was prepared by using 12.5 times as much TCD as in Sample 1 but without lampblack. In this case both the filler and pigment qualities are examined. The evaluation involved a drawdown comparing samples 1 and 2 with a standard paint. Examination of the drawdown results show that for both samples the tinting strength was somewhat below standard. If sufficient TCD

added to match the tinting strength level of the standard, the resulting product would be applicable as a pigment extender. It was clear that further research and development are necessary to ascertain the variation of tinting strength with the carbon content of TCD and with the behavior of TCD-lampblack mixtures. It appears that for paint application, size and carbon content are important but that the source of the TCD is unimportant.

Rubber

The pyrolyzed manure ash (TCD) has been successfully substituted for carbon black and filler in rubber. The TCD was prepared in a manner similar to that previously described for ink and paint applications. It was ball milled to a particle size between 1 and 25 microns. Particle sizes in excess of this range are unacceptable for rubber applications.(1)

Eight rubber companies as well as the Rubber Tehhnology Laboratory of the University of Southern California were contacted concerning the evaluation of TCD as a filler and pigment for rubber. Only the Da-Pro Rubber Company and the University of Southern California were willing to evaluate the TCD samples. The rubber samples made up by both laboratories appear to be inferior to existing rubber made with carbon black. The general conclusion is that the particle size of TCD was too large and that residual salts and other unknown constituents in TCD were the main causes of its inferior performance.

Rubber samples prepared with TCD were compared to samples of standard rubber. The TCD was added to totally replace the carbon black content. The typical batch formulation of the TCD rubber is given below:

ethylene propalene rubber	100 gms
naphtenic oil	25 gms
stearic acid	1 gm
ZnO	5 gms
TCD	50 gms
petrolatum	3 gms
sulphur (for curing)	1.5 gms
curative agent (accelerator)	2.34gms

The examination indicated that the high level of impurities in the TCD caused sponginess and blistering of the raw batch. The impurities essentially arise from the low temperature pyrolysis conditions used to obtain a high carbon content. The particle size was deemed adequate for filler purposes but was much too coarse to be used as a carbon black substitute. Thus, the sample fabricated by Da-Pro, where TCD was substituted for carbon black, possessed inferior properties to a standard rubber specimen (i.e., with carbon black). The samples evaluated contained the highest content of carbon (about 30%). Samples made with less than 30% carbon are unacceptable as a black pigment. However, the carbon content is unimportant as far as filler application is concerned.

The Shore hardness value (scale A) was 43 as compared to the standard sample's value of 55. Tensile strength of the standard was 9.8×10^4 bm/cm^2. Thus the rubber could technically be used in non-critical applications which require low stress levels, e. g., rubber mats, automotive stripping, and certain types of hosing. However, the problems of blistering and sponginess must be solved before utilization is viable.

The conclusion reached by this industrial evaluation was that TCD can be successfully used as a filler material in rubber. It may be substituted for clay, but this requires that the TCD be totally pyrolyzed so that all traces of nitrogen are removed. For this case, the carbon content is unimportant and high temperature pyrolysis is required. The carbon may be driven off into the oil fraction. A preliminary analysis indicates that TCD is economically competitive with washed clay as a filler in rubber.

In conclusion then, TCD holds promise only as a filler material in certain types of rubber. Its low carbon content was inferior to lamp-black as a pigment. Again the varying sources of manure were not an important factor.

Tile

TCD may be utilized as a filler in a ceramic tile replacing the conventional fillers. The tiles produced using TCD as a filler are odorless, waterproof, durable, strong, hard, and incombustible. They can be made in a variety of colors and decorative patterns by adding different materials to the tile surface during manufacture.

Physical properties such as density, moisture absorption, bending strength, and impact strength compare favorably with conventional materials.

The process of manufacturing these tiles consists of uniformly blending the ball-milled, carbonaceous aluminosilicate residue (TCD) with powdered waste glass (from bottles and jars) then heating the mixture while it was contained in a mold. the processing temperature varies from 700° C to 900° C, depending upon thickness. Once the mold and mixture has reached temperature, the mold was removed from the kiln and a pressure of approximately 3.5×10^4 gm/cm^2 is applied. The pressure during the heat treatment was used to coalesce the homogeneously-mixed TCD filler with the glass, so that they were fused together into a single mass. Tile properties were tested. Their characteristics are listed in Table 5.

Table 5. PROPERTIES OF HOT-PRESSED TILES

Density, controllable	1.8 to 2.4 g/cm^3
Incombustible	Class A
Flexural strengths	4.2×10^5 to 5.6×10^5 grams/cm^2
Apparent impact strength	128 Newton-meters at 1.8g/cm^3, density
Abrasion wear index (Taber)	55 to 130 (minimum acceptable is 35)
Moisture absorption as per CTI (Ceramic Tile Institute) Standard 32-12	2.2% at 1.8g/cm^3 density
Wt. per area	1.95 grams per square centimeter .95 cm thickness
Hardness, Moh scale	6
Decoration	bulk and surface colors possible; glazed easily
Miscellaneous	can be painted, glued, non-toxic and odorless

Charcoal Briquettes

Charcoal Briquettes can be made with TCD. The pyrolyzed ash can be used directly out of the pyrolyzer without any further size reduction. A 1% corn starch solution is used as a binder. The solution is mixed with the TCD and put into a mold which is then pressed to about 3.5 to 7.0 x 10^4 gm/cm^2. The compacted mass was then allowed to dry. Small scale production with a laboratory press and a commercial 1.8 x 10^5 kg briquetting press has been achieved.

One field of use found for charcoal briquettes besides commercial uses was the use of the briquettes as a fuel supplement in coal-fired utuilities. Presently, the only fuel supplement used in the cellulosic fraction of municipal solid wastes. Cellulosic wastes are extremely awkward to handle, due to bulkiness. Samples of TCD briquettes were sent to the Union Electric Co., St. Louis, Mo., which uses fuel supplements. As of this date, the evaluation was not carried out due to a long strike at Union Electric Co. Experiments indicate that one drawback could be the extremely high ash content (70%-80%) of the briquettes. Its briquetted form lends itself to easy handling, transportation, and storage.

In only qualitative field tests, the TCD briquettes were compared against a commercial brand of charcoal briquettes. It was noted that the TCD briquettes lighted with relative ease and reached maximum temperature much sooner, although they did not reach as high a temperature nor did they sustain their temperature as long. No odors of manure or any other foul odors were emitted during their combustion. Food was actually cooked over these briquettes and no unusual taste was noted. Because of its high ash content, the largest use of the TCD briquette would be as a fuel supplement in the newer stirred-bed, coal-fired utuilities and gasifiers. The ash would not be a problem in stirred-bed, coal-fired utilities and gasifiers or in a stirred-bed, coal-fired boiler (2).

Foaming Agent

In work performed prior to this grant, TCD was used as a foaming agent in the fabrication of lightweight foamed glass. The TCD was milled to a minus two hundred mesh particle size and mixed with glass powder. This mixture was put

in a mold and fired to a temperature at which the glass softens. At these temperatures, the TCD decomposes and the gas generated creates small pores in the softened glass. Upon cooling, the small pores are trapped and a cellular structure results. The light-weight glass foam has potential as a good acoustical and thermal insulator for building applications. Details of foamed glass can be found in patents 3,811,851 and 3,900,303.

PRODUCT APPLICATIONS OF THE OIL FRACTION

The oil fraction collected from the pyrolysis treatment has been described in Section V. Such TCD oil appears to have potential in two different applications. One is the direct use as a crude oil while the other involves the fabrication of carbon black from crude oil. Each of these applications is discussed below.

Crude Oil

The liquid fraction accumulated by condensing the vapor emitted during pyrolysis can be separated into an oil fraction and an aqueous fraction by centrifuging.

This crude oil has a chemical composition which essentially resembles that of natrual crude oil. The chemical composition is not primarily dependent on the origin of the manure but on the pyrolysis process. Preliminary evaluations suggest that the TCD crude oil can be readily used as a fuel oil. Early work by Chevron Oil Company also indicated that it can be fractionated into various petroleum products.

Oil companies contacted included the Union Oil Company, Standard Oil Company, Gulf Oil Company, and Shell Oil Company. These companies indicated that because of the relatively small quantities of TCD crude oil which can ultimately be produced as compared to oil from natural sources, they have little interest in evaluating the material at present.

The subsequent utilization of TCD oil is thus wholly dependent on the economics of mass production. It appears that in the future, if pyrolysis of manure will be carried out at feedlots on a large scale, small, local, independent industries must be contacted to exploit the utilization of the TCD oil as a heating fuel.

Because of the limited quantity as compared to present natural oil, the possibility of its use in fractionation into various hydrocarbons, such as gasoline, with refineries is remote.

Carbon Black Production from TCD Oil

Carbon black has been produced on a laboratory scale from the TCD crude oil. Information was provided by Cities Service Co., Petrochemical Research Division, (Mojave, Calif.) on carbon black production. The TCD crude oil has been converted to carbon black using such basic production methods. Carbon black was produced by the incomplete combustion of the oil vapor (4).

Two methods of obtaining carbon blacks were tried (Figure 7).

Open Pan Burning –

This consisted of igniting an open pan of oil in an enclosed hood, leading to filter and exhaust equipment.

Furnace Blacks –

Furnace blacks were produced by incomplete combusion of oil vapor. A cure, small-scale, carbon black production furnace was made in the laboratory by using pipes and pipe fittings. Oil spray was mixed with a gas-rich air mixture and ignited. The quench action of the steam created the incomplete combustion of the mixture. Carbon black was then collected by a filter.

Small samples of carbon black collected from both of these methods were tried in ink and then evaluated by an independent ink manufacturer (Gans Ink). The carbon black was comparable in quality to commercial carbon black. For example, the ash content was less than 1% and the average particle size by electron microscopy was essentially the same as that of commercial furnace black. The ink made was entirely acceptable. It would appear that such TCD oil-carbon black will be satisfactory as a replacement for commercial carbon black in every application.

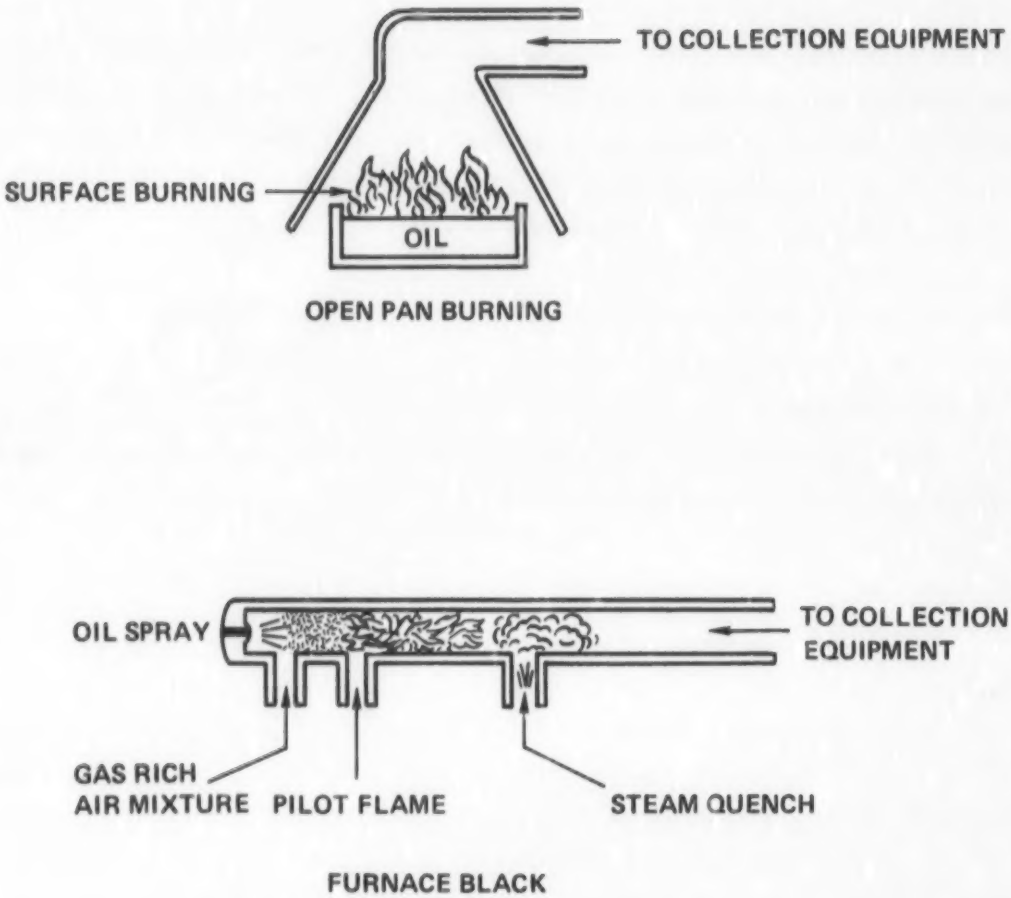


Figure 7. Methods of Converting Crude Oil to Carbon Black.

PRODUCT APPLICATION OF AQUEOUS FRACTION

The liquid fraction condensed during pyrolysis can be separated into an oil fraction and a water fraction. The water fraction holds promise as a fertilizer. This application is virtually the only one identified thus far for the aqueous portion.

The liquid fraction was centrifuged at 1,500 revolutions per minute for five minutes to separate the oil and water. The water was then passed through filter paper to remove some of the finer suspended solids. The sample was then sent to Arizona Agrochemical, Phoenix, Arizona, for analysis and evaluation of its potential as a fertilizer. The analysis is shown in Table 6. They found that the liquid did not have sufficient fertilizer value with respect to primary nutrients (nitrogen, phosphorus, and potassium). The company suggested upgrading the liquid with these elements added from other sources, and it would then be suitable for fertilizer applications. In its present state, the aqueous fraction could be used as a carrier for primary nutrients. In this case, the liquid was used in place of water, and the few components present (Table 6) were obviously of greater nutrient value than water. For on-farm tests, substantially larger batches were needed (in excess of approximately 400 liters).

Table 6. NITROGEN CONTENT ANALYSIS OF AQUEOUS FRACTION

% Total Nitrogen (N)	0.82
% Organic Nitrogen (N)	0.79
% Nitrate Nitrogen (N)	0.03
% Ammoniacal Nitrogen (N)	0.44
% Available Phosphoric Acid (P_2O_5)	<0.02
% Potash (K_2O)	0.03
% Total Sulfur (S)	0.05
% Total Soluble Salts	2.10
pH	8.05

The equipment was inadequate to furnish such large quantities. It is evident that a more efficient condensing system would significantly upgrade the aqueous fraction in nitrogen content. The nitrogen "accountability ratio" (Table 3) was lowest of all elements because of difficulty in condensing the nitrogen containing volatiles. The value of this aqueous fraction will undoubtedly be much enhanced when an improved condensing system is incorporated in the pyrolyzer. For instance, in earlier, very small-scale, controlled experiments, a nitrogen content as much as 11.6% was noted.

SECTION VII

COST ANALYSIS

PRODUCT COSTS

The optimum conditions of pyrolysis are dependent upon the desired by-product. From this report it is evident that the use of the TCD as a carbon black substitute and filler is likely to bring the greatest return on investment. For these applications the manure is pyrolyzed at relatively low temperatures. The cost of producing pyrolyzed ash has been estimated. For a plant to process approximately 2.72×10^7 kg (30,000 tons) of manure (25 percent water) per year, the cost of the ash is on the order of \$3.50 to \$4.00 per 9.08×10^2 kg (ton). The crude oil is taken as a credit against costs. For the carbon substitute and filler applications, size reduction is necessary. A maximum total cost of \$10 per 9.08×10^2 kg (ton). The crude oil is taken as a credit against costs. For the carbon substitute and filler applications, size reduction is necessary. A maximum total cost of \$10 per 9.08×10^2 kg (ton) is estimated to produce the highly carbonaceous residue in a form of fine powder, nearly as fine as carbon black. Current rubber filler substitutes sell for approximately \$.015 per .45 kg (pound). If fine carbonaceous ash were sold for approximately the same price, the net return would be on the order of \$20 per 9.08×10^2 kg (ton). The above analysis clearly indicates that the pyrolyzed ash may be a viable, economically successful product when used as a carbon black substitute or filler.

DRYING COSTS

The pre-drying of the manure (assumed 25 percent water) does not present much of an economic problem. In the reported experiments, manure was predried in a small chamber on top of the pyrolysis unit. The flue gases from the pyrolyzer were used to dry the wet manure. In a large tonnage application, a direct heat rotary unit could be installed before the feed mechanism to the pyrolyzer. Utilizing the exhaust flue gases of the pyrolysis furnace, the manure can be thoroughly dried. In this case, the only additional energy expenditure associated with drying would be the electrical requirement needed to turn the rotary drier unit. This cost is slight (\$.10 to \$.12 per 9.08×10^2 kg).

SECTION VIII

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SECTION IX

PUBLICATIONS AND INVENTIONS

A paper entitled: "Product Applications of Treated Livestock Waste," was presented at the International Symposium on Livestock Wastes at the University of Illinois April 23, 1975. The paper will be published in the Symposium Proceedings. An abstract of this paper was previously submitted to EPA.[2] The support provided by EPA was gratefully acknowledged.

"Invention Disclosure" forms were submitted for the pyrolysis equipment developed during this project. The title is "Apparatus for Pyrolyzing Cattle Manure" with B. Dunn and E. Tseng as co-inventors. This disclosure was submitted to Mr. F.L. Meadows, Chief, Grants Operations Branch, EPA, Washington, D.C. 20460, by Miss Josephine Opalka, Patent Administrator of the University of California on August 19, 1975.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The purpose of the project was to design and build a pyrolysis apparatus for cattle manure and to investigate the potential uses of the pyrolysis by-products. A pyrolysis machine of semi-continuous feed capabilities was designed and built. Various conditions of pyrolysis treatments were investigated and their influence on the amount and composition of the by-products determined. High carbon residues were found to require lower pyrolysis temperatures. The carbon content of these residues appeared to be unaffected by the geographic location of the original manure. Contact with interested parties and appropriate industries who could be prospective users of each of the products was initiated to obtain their technical expertise in evaluating these products. The pyrolysis by-products seem to have some potential industrial applications. These by-products include the solid residue, an oil fraction, and an aqueous fraction. The solid residue may serve as a carbon black substitute or as a filler material in rubber, ink, and paint. The aqueous fraction collected during pyrolysis has been evaluated for fertilizer applications.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Cattle; Agricultural Wastes; Pyrolysis; By-Products	Lampblack, Glass Foam; Ink; Glass Tile; Rubber; Briquettes; Oil; Fertilizer; Paint	02/A, C, E

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